KINETICS

1. An environmental concern is the depletion of O_3 in Earth's upper atmosphere, where O_3 is normally in equilibrium with O_2 and O. A proposed mechanism for the depletion of O_3 in the upper atmosphere is shown below.

Step I $\quad O_3 + C1 \Rightarrow O_2 + C1O$

Step II $\quad C1O + O \Rightarrow C1 + O_2$

(a) Write a balanced equation for the overall reaction represented by Step I and Step II above.

(b) Clearly identify the catalyst in the mechanism above. Justify your answer.

(c) Clearly identify the intermediate in the mechanism above. Justify your answer.

(d) If the rate law for the overall reaction is found to be, *rate* = $k[O_3][C1]$, determine the following.

(i) The overall order of the reaction

(ii) Appropriate units for the rate constant, k.

(iii) The rate-determining step of the reaction, along with justification for your answer.

2.

$$2\ ClO_{2(g)} + F_{2(g)} \Rightarrow 2\ ClO_2F_{(g)}$$

The following results were obtained when the reaction represented above was studied at 25°C.

Experiment	Initial $[ClO_2]$, $(mol \cdot L^{-1})$	Initial $[F_2]$, $(mol \cdot L^{-1})$	Initial Rate of Increase of $[ClO_2F]$, $(mol \cdot L^{-1} \cdot sec^{-1})$
1	0.010	0.10	$2.4\ 10^{-3}$
2	0.010	0.40	$9.6\ 10^{-3}$
3	0.020	0.20	$9.6\ 10^{-3}$

(a) Write the rate law expression for the reaction above.

(b) Calculate the numerical value of the rate constant and specify the units.

(c) In experiment 2, what is the initial rate of decrease of $[F_2]$?

(d) Which of the following reaction mechanisms is consistent with the rate law developed in (a). Justify your choice.

I. $ClO_2 + F_2 \quad ClO_2F_2$ (fast)
$ClO_2F_2 \Rightarrow ClO_2F + F$ (slow)
$ClO_2 + F \Rightarrow ClO_2F$ (fast)

II. $F_2 \Rightarrow 2\ F$ (slow)
$2\ (ClO_2 + F \Rightarrow ClO_2F)$ (fast)

3. Consider the following general equation for a chemical reaction.

$$A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)} \qquad \Delta H^0 \text{ reaction} = -10 \text{ kJ}$$

(a) Describe the two factors that determine whether a collision between molecules of A and B results in a reaction.

(b) How would a decrease in temperature affect the rate of the reaction shown above? Explain your answer.

(c) Write the rate law expression that would result if the reaction proceeded by the mechanism shown below.

$A + B \quad [AB]$ (fast)

$[AB] + B \Rightarrow C + D$ (slow)

(d) Explain why a catalyst increases the rate of a reaction but does not change the value of the equilibrium constant for that reaction.

4. Graphical methods are frequently used to analyze data and obtain desired quantities.

(a) $2\ HI_{(g)} \Rightarrow H_{2(g)} + I_{2(g)}$

The following data give the value of the rate constant at various temperatures for the gas phase reaction above.

T (K)	*k* (litre/mol sec)
647	$8.58\ 10^{-5}$
666	$2.19\ 10^{-4}$
683	$5.11\ 10^{-4}$
700	$1.17\ 10^{-3}$
716	$2.50\ 10^{-3}$

Describe, without doing any calculations, how a graphical method can be used to obtain the activation energy for this reaction.

(b) $A_{(g)} \Rightarrow B_{(g)} + C_{(g)}$

The following data give the partial pressure of A as a function of time and were obtained at 100°C for the reaction above.

P_A (mm Hg)	t (sec)
348	0
247	600
185	1200
105	2400
58	3600

Describe, without doing any calculations, how graphs can be used to determine whether this reaction is first or second order in A and how these graphs are used to determine the rate constant.